Radiochemical Analysis of 3H, 14C, 55Fe, 63Ni in Waste and Environmental Samples

Hou, Xiaolin

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Radiochemical Analysis of ^{3}H, ^{14}C, ^{55}Fe, ^{63}Ni in Waste and Environmental Samples

Xiaolin Hou

Risø National Laboratory for Sustainable Energy ,
Technical University of Denmark

Radionuclides in the nuclear waste

- Gamma radionuclides

  ^{60}Co, ^{133}Ba, $^{152,154,155}Eu$, ^{137}Cs, ^{134}Cs, ^{106}Ru

- Beta Emitter

  ^{3}H, ^{14}C, ^{63}Ni, ^{55}Fe , ^{36}Cl, ^{41}Ca, ^{90}Sr, ^{99}Tc, ^{129}I, ^{135}Cs, ^{94}Nb

- Alpha emitter (transuanics)

  $^{238\text{-}241}Pu$, ^{241}Am, $^{234,244}Cm$, ^{237}Np

Waste samples and the relevant critical radionuclides in the decommission

- Graphite (reactor)
  - ^{3}H, ^{14}C, ^{55}Fe, $^{63, 69}Ni$, ^{36}Cl, ^{152,154} Eu, ^{90}Sr, ^{137}Cs, ^{99}Tc
- Concrete (normal or heavy)
  - ^{3}H, ^{14}C, ^{41}Ca, ^{133}Ba, ^{36}Cl, ^{60}Co, ^{41}Ca, ^{133}Ba, ^{134}Cs, ^{3}H, ^{14}C, ^{36}Cl, ^{60}Co, ^{55}Fe, $^{63, 69}Ni$, transuranics
- Steel/stainless steel
  - ^{60}Co, ^{55}Fe, $^{63, 69}Ni$, ^{36}Cl, ^{152,152} Eu, ^{65}Zn, ^{151}Sm
  - ^{60}Co, ^{55}Fe, $^{63, 69}Ni$, ^{36}Cl
- Lead
  - ^{133}Ba, ^{60}Co, ^{63}Ni
- Ion exchange resin
  - ^{137}Cs, ^{60}Co, ^{55}Fe, ^{63}Ni, ^{59}Ni, ^{14}C, ^{90}Sr, ^{129}I, ^{135}Cs, ^{99}Tc, transuranics

Tritium and ^{14}C *in the Environment*

- Sorce:
  - Nuclear weapons testing in 1960's
  - Discharge fron reprocessing plants
  - Discharge from nuclear power plants

- Investigation of Tritium and ^{14}C in the environment
  - Measurement of the contamination level from nuclear facility
  - ^{14}C dating
- Environmental Samples
  - Water
  - plants (seaweed, grass, lichen, fish.)
  - soil, sediment

^{55}Fe and ^{63}Ni in the Environment

- Sorce:
  - Nuclear weapons testing in 1960's
  - Discharge fron reprocessing plants
  - Discharge from nuclear power plants

- Investigation of ^{63}Ni and ^{55}Fe in the environment
  - Measurement of the contamination level from nuclear facility
  - Using ^{55}Fe and ^{63}Ni released from nuclear facility as a tracer to study their environmental and chemical behaviours
- Environmental Samples
  - Water
  - plants (seaweed, grass, lichen, fish.)
  - soil, sediment

Content

- Rapid analytical method for the determination of ^{3}H and ^{14}C in graphit and concrete, and other solid samples

- Analytical method for the determination of ^{63}Ni, ^{55}Fe in waste samples (Steel, Al, lead, graphite and concrete) and environmental sample

Determination of ^{3}H and ^{14}C in graphite and concetre

- *Production of ^{3}H in reactor*
  - $^{2}H\ (n, \gamma)^{3}H$
  - $^{6}Li(n, \alpha)^{3}H$
  - $^{3}He(n, p)^{3}H$

- *Production of ^{14}C in reactor*
  - $^{13}C(n, \gamma)^{14}C$
  - $^{14}N(n, p)^{14}C$
  - $^{17}O(n, \alpha)^{14}C$

Properties of C-14 and H-3

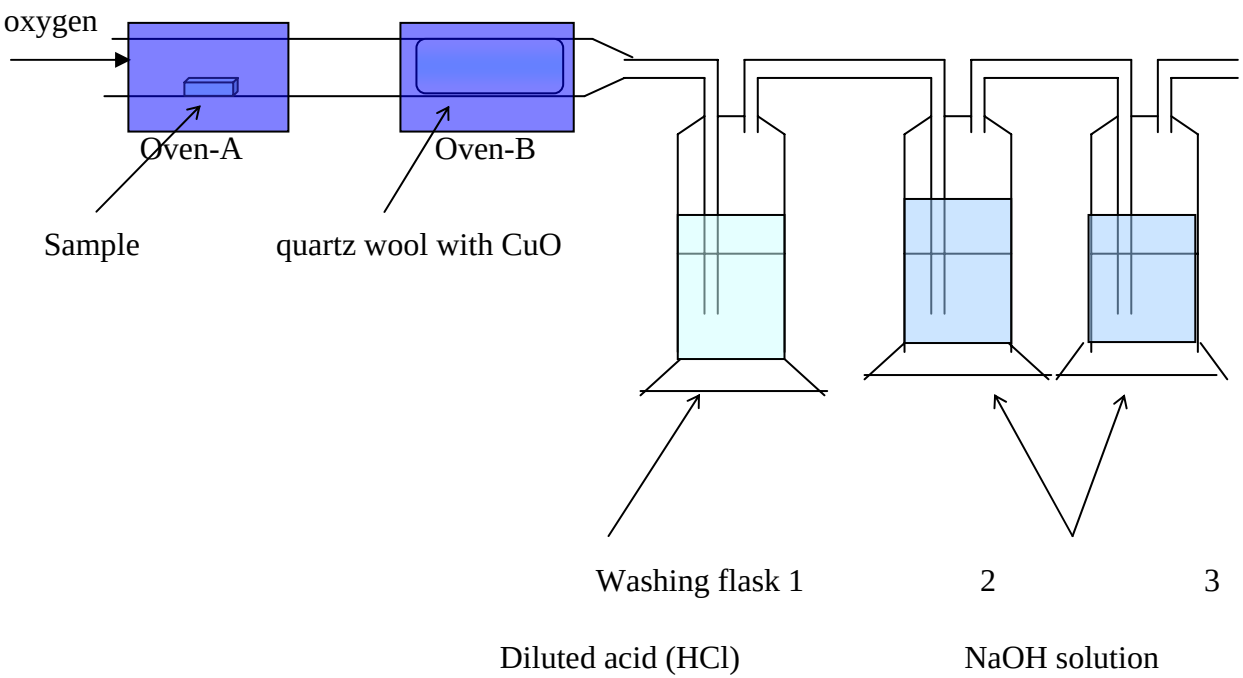
Nuclides	Half life	Decay	Energy, keV	Measurement
^{3}H	12.35 y	β	18.6	LSC
^{14}C	5736 y	β	156	LSC

Measurement of C-14 and H-3

- Low energy
  Liquid Scintilation Counter
- Continueous epectrum
  Separation before measurement

Separation of ^{3}H, ^{14}C from soild waste by combustion method

- Flask 1: ^{3}H, ^{129}I, ^{99}Tc
- Flask 2,3: ^{14}C, ^{129}I



Disadvantage of these method for the determination of ^{14}C and ^{3}H

- Time consumming: (3-4 hours is needed for decomposition of sample and 1-2 hours for separation and purefication of ^{14}C and ^{3}H in the absorbed solution.)
- Additional purfication procedure is needed.
- Worse detection limit, due to large volume of absorption solution
- High quench, due to high concentration acid or alkali solution is used.
- High risk acid (perchloric acid) is used.

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Rapid separation of ^{3}H and ^{14}C waste samples by combustion using Packard Oxidizer

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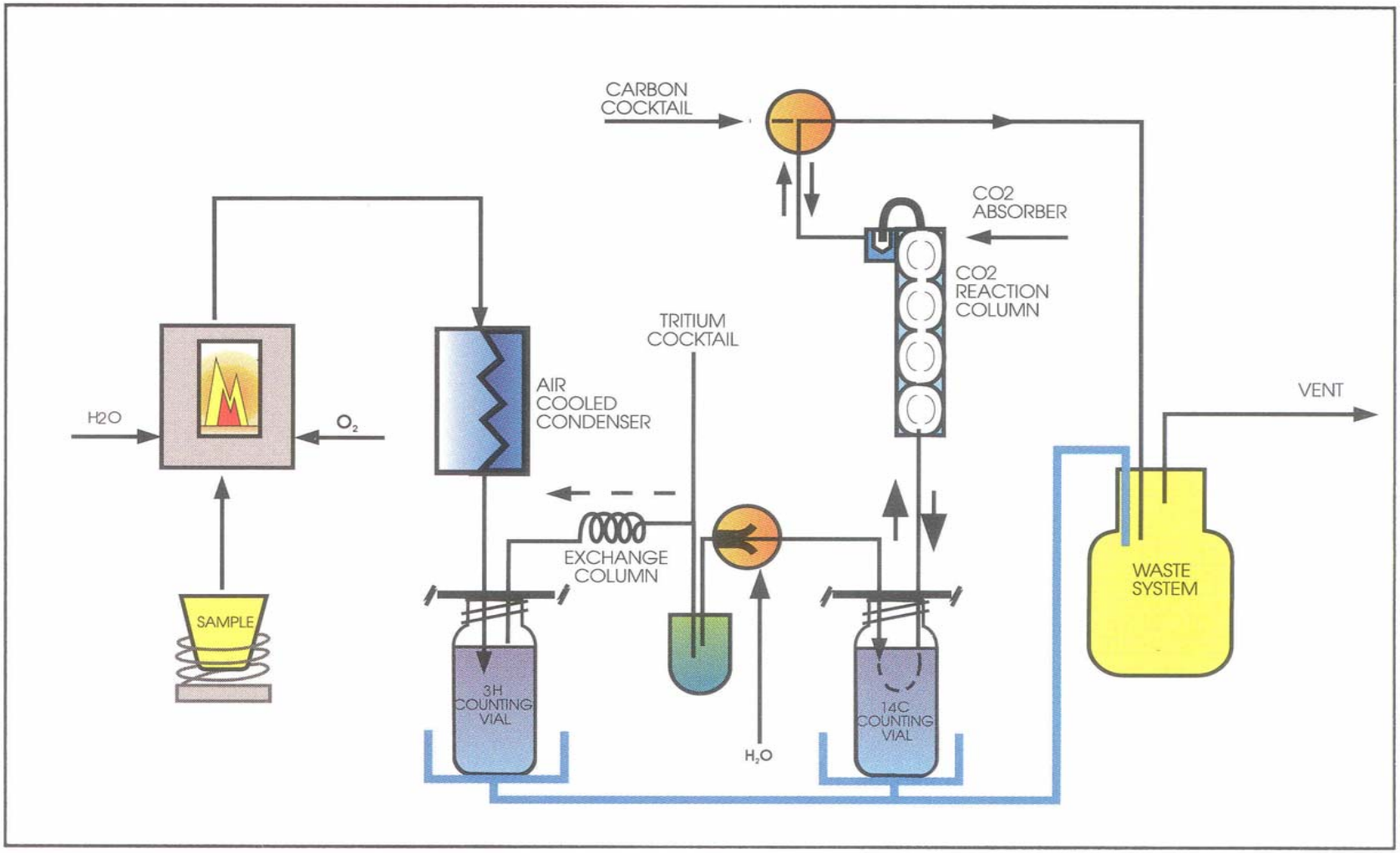


Problems?

- Cross contamination
- Efficiency of combustion (recovery)
- Impurity nuclides in separated fractions

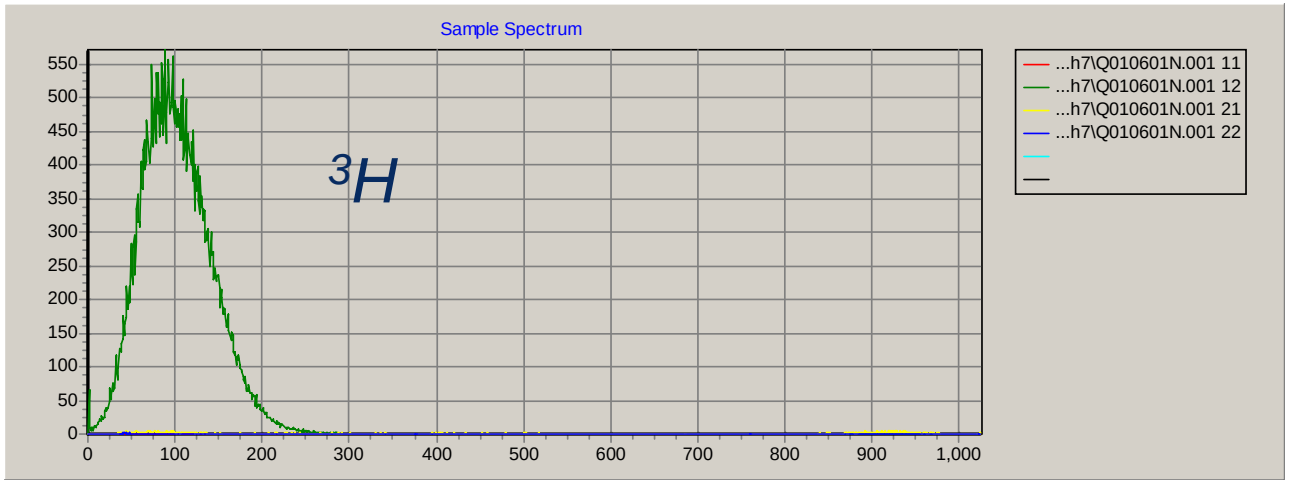
DTU

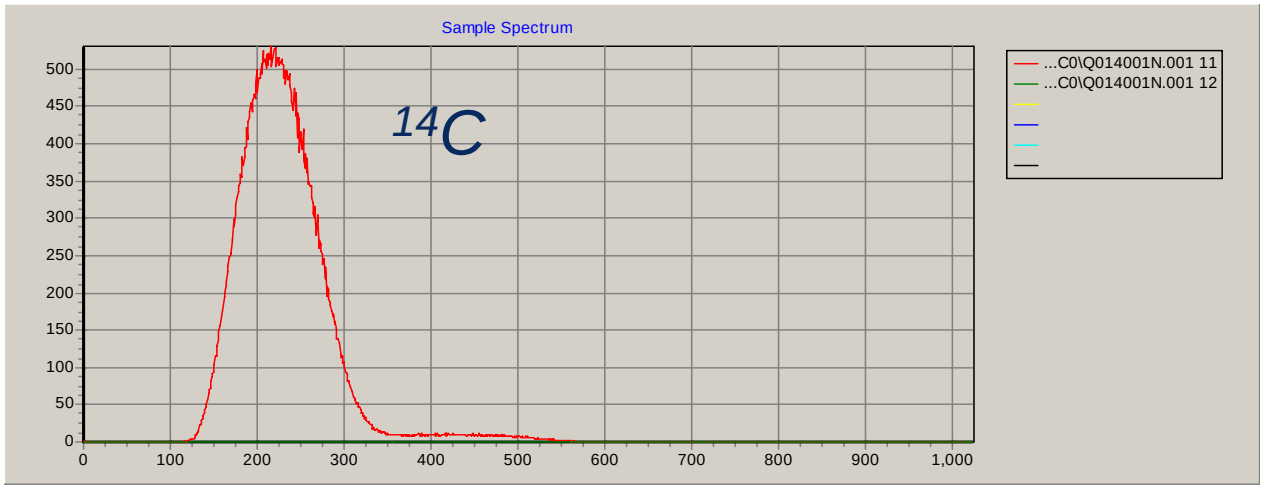
RISØ

Decomposition of graphite and concrete for release C-14 and H-13 using Oxidizer

sample	weight	^{3}H added	^{14}C dded	^{3}H counts	^{14}C counts	Recovery or memory of ^{3}H,	Recovery or memory of ^{14}C
	mg	Bq	Bq	CPM	CPM	%	%
graphite	106.03	0	0	10	12		
graphite	55.95	0	0	16	13		
graphite	41.2	0	0.47	11	13925	0.01	94.09
graphite	30.03	0	1.46	25	60960	0.02	105.50
graphite	34.76	0.4	0	12083	20	96.21	0.16
graphite	38.27	4.87	0	115038	24	93.07	0.02
concrete	35.23	0	0.47	16	12292	0.10	97.87
concrete	41.57	0	2.92	27	119809	0.02	96.93
concrete	38.35	0.4	0	12338	26	98.24	0.2
concrete	37.63	4.87	0	124118	28	100.42	0.02

Beta spectrum of ^{3}H and ^{14}C measured by Quantulus Liquid Scintillation Counter



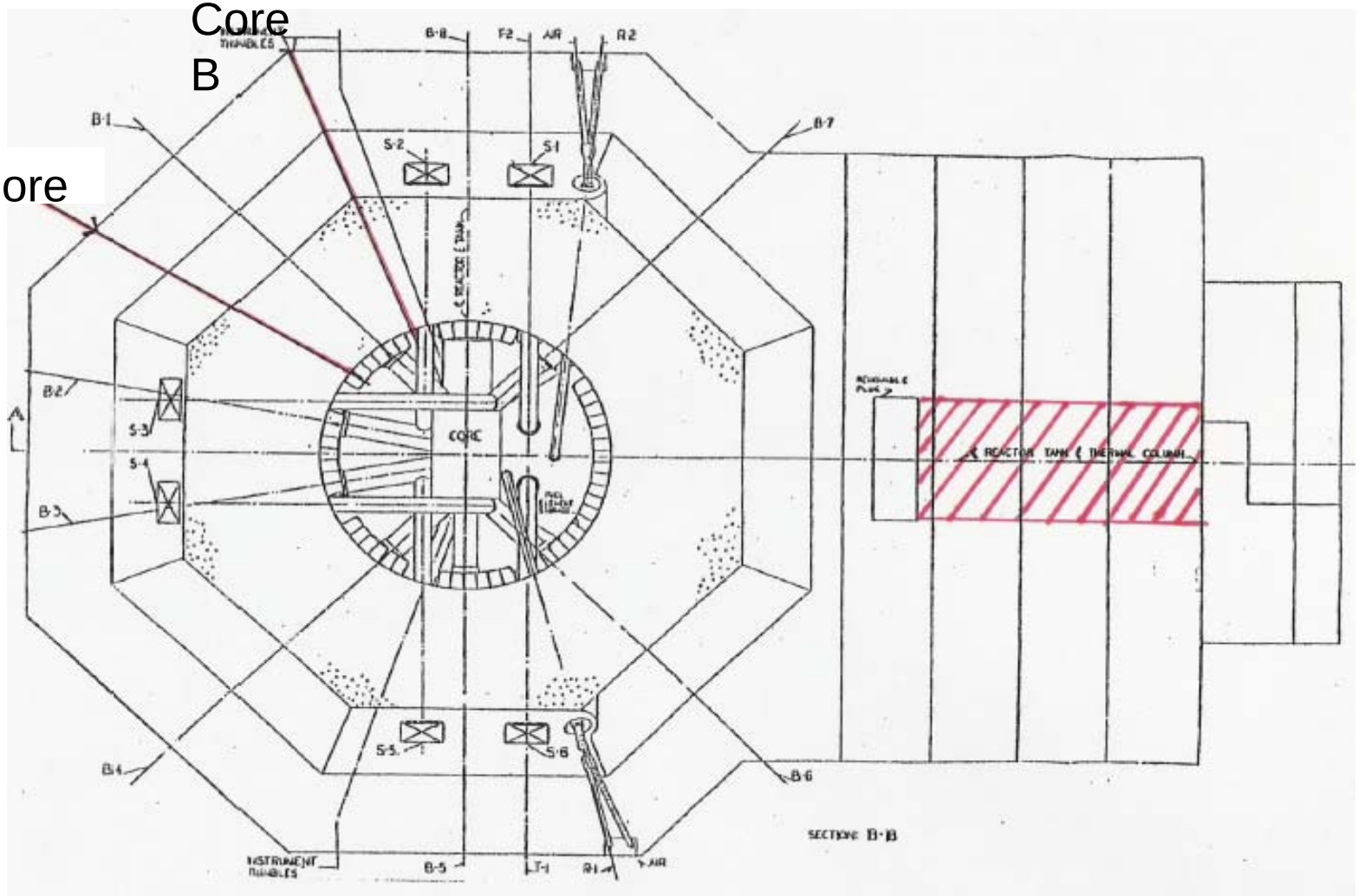


No other impurity nuclides were seen in the H-3 and C-14 spectrum

Detection limits for C-14 and H-3

- For graphite, 0.1 gram sample can be directly decomposed, the detection limits of ^{14}C and H-3 can be calculated to be: 0.7 and 0.5 Bq/g.

- For Concrete, 0.3 gram sample can be decomposed, the detection limits of C-14 and H-3 are 0.23 and 0.18 Bq/g



Sampling of concrete and graphite from danish reactor, DR-2

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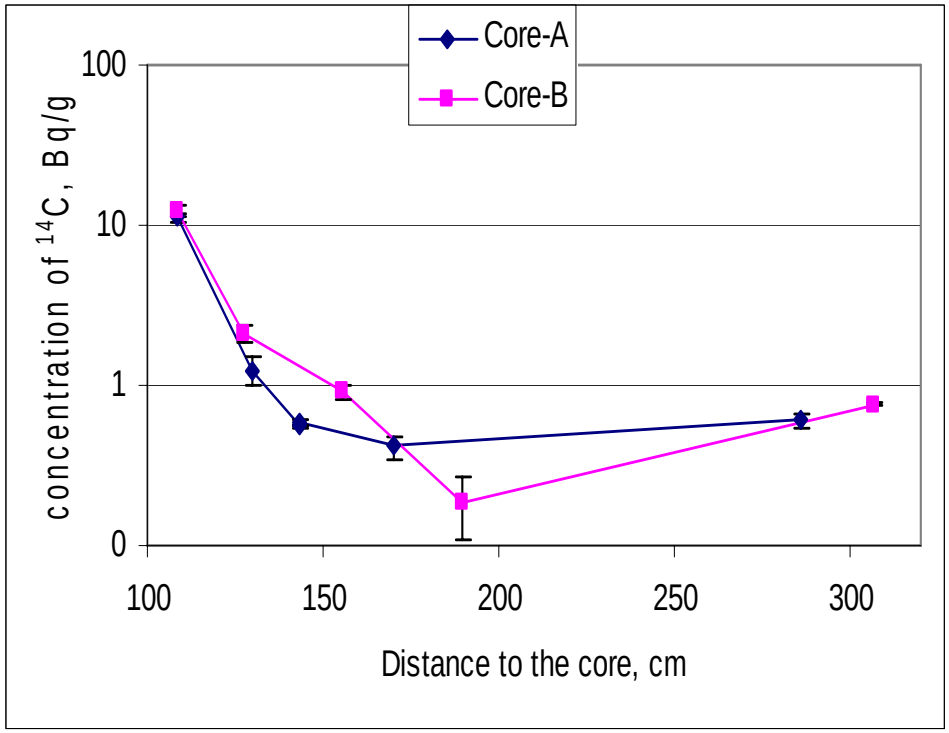
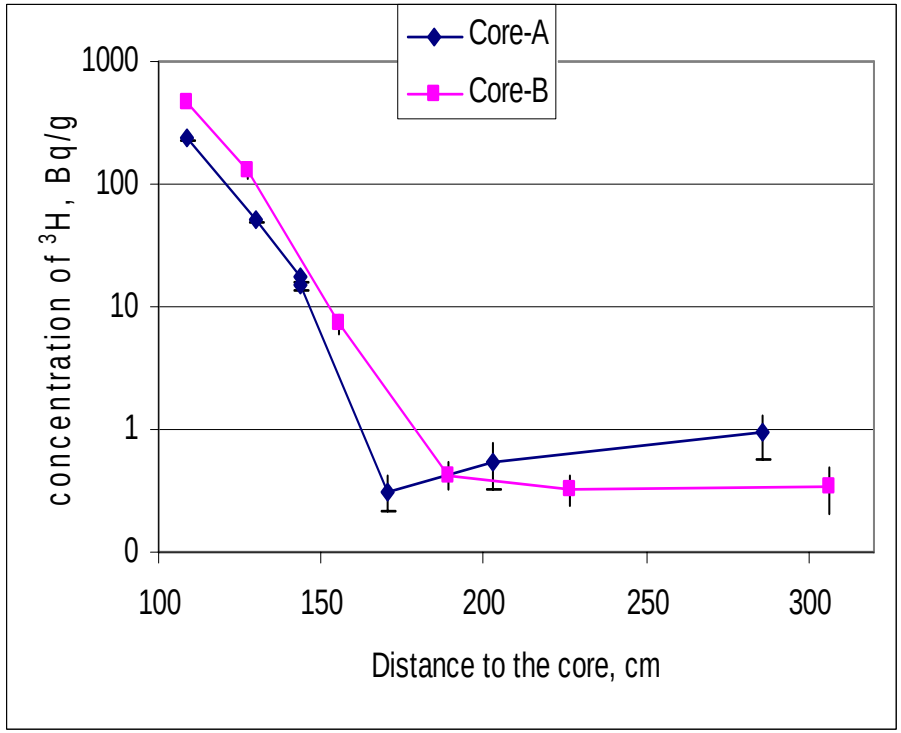
Analytical Results of ^{3}H and ^{14}C in 9 graphite samples

Code	^{3}H, Bq/g		^{14}C, Bq/g	
	Average	SD %	Average	SD %
TK5.5 Yi	2.12E+02	4.50	4.70E+03	17.33
TK5.5 Yy	7.55E+03	2.85	1.97E+05	11.48
TK5.5 Ii	1.96E+04	2.43	1.04E+06	10.36
TK5.5 Iy	9.04E+03	3.01	4.31E+05	0.93
TK7.5 Yi	2.67E+04	2.19	1.11E+06	3.39
TK7.5 Yy	1.08E+04	1.74	3.67E+05	7.88
TK7.5 Ii	1.46E+04	2.76	9.31E+05	5.53
TK7.5 Iy	6.77E+03	1.61	3.44E+05	9.66
Sample-G	3.21E+03	1.25	7.16E+04	11.73

^{3}H and ^{14}C in heavy concrete in Danish reactor DR2





Production of ^{63}Ni and ^{55}Fe in Nuclear Reactor (neutron activation)

- ^{63}Ni:
  - ^{62}Ni(n, γ)^{63}Ni (σ=14.5 b; η_{62Ni}=3.63%)
  - ^{63}Cu(n, p)^{63}Ni, (η_{63Cu}=69.17%)
- ^{55}Fe:
  - ^{54}Fe(n, γ)^{55}Fe (σ=2.3 b; η_{54Fe}=5.85%)
  - ^{56}Fe(n, 2n)^{55}Fe, (η_{56Fe}=91.75%)

Decay of ^{63}Ni and ^{55}Fe

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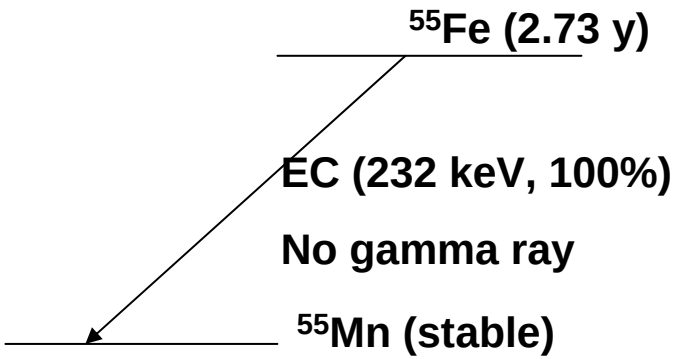
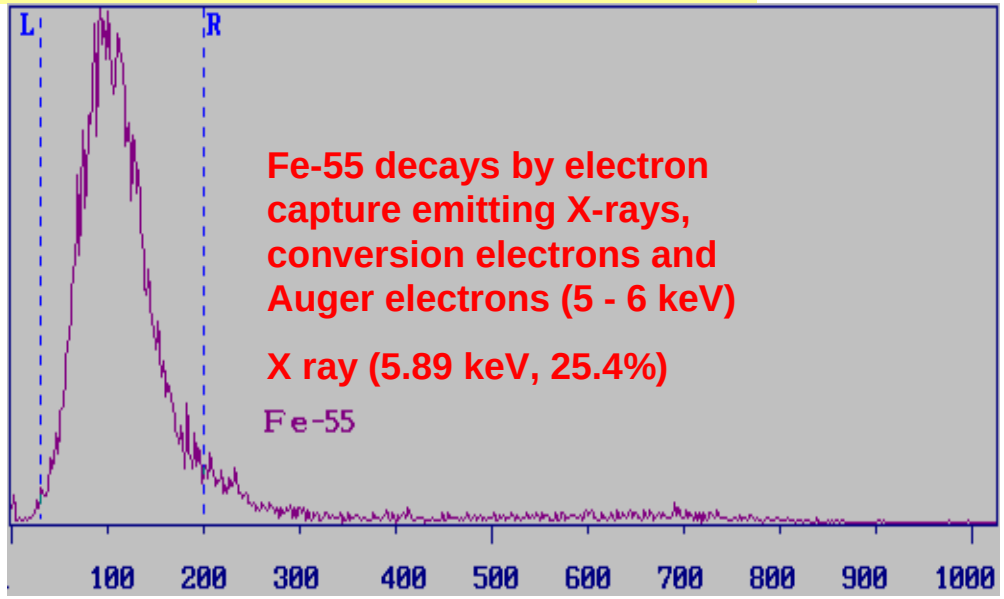
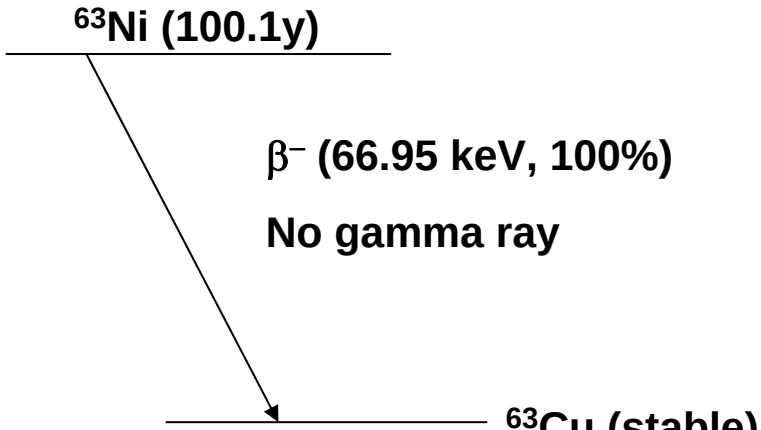
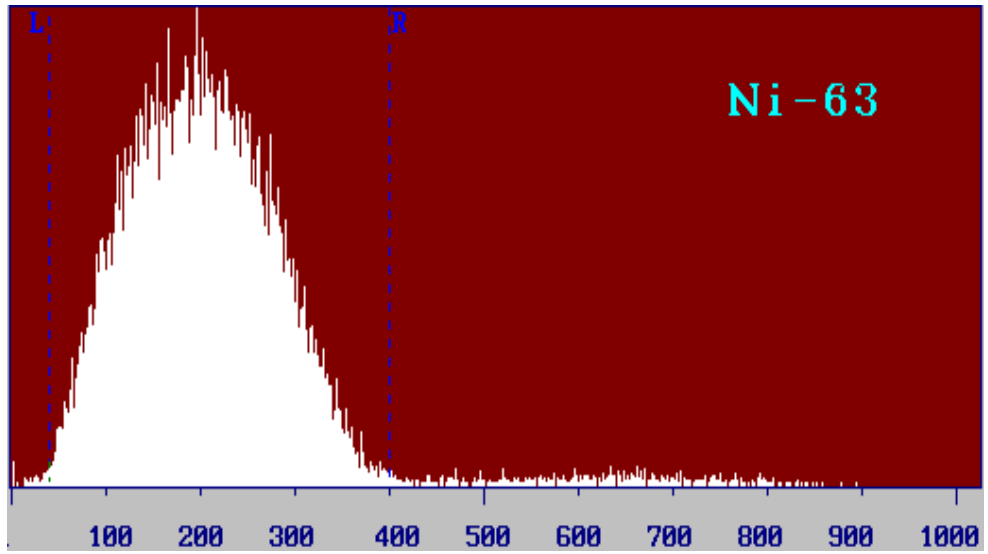








Neutron activation products of Fe and Ni

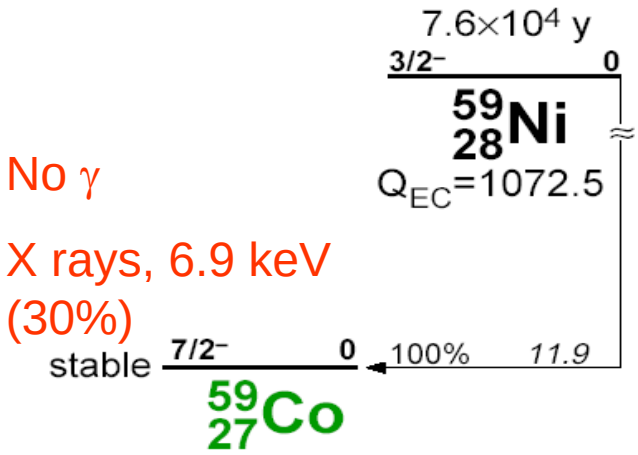
Target nuclide	Abundance %	(n, γ) cross section	Activation product	Half life	Decay
^{58}Ni	68.3	4.64	^{59}Ni	7.6x10^{4} y	EC (Kx=6.9 keV)
^{60}Ni	26.1	2.82	^{61}Ni	Stable	
^{61}Ni	1.13	2.51	^{62}Ni	Stable	
^{62}Ni	3.59	14.25	^{63}Ni	100 y	β-, 66.9 keV
^{54}Fe	5.85	2.3	^{55}Fe	2.73 y	EC
^{56}Fe	91.75	2.6	^{57}Fe	stable	
^{58}Fe	0.28	1.31	^{59}Fe	44.5 d	β-, γ

Atomic ratio: ^{59}Ni/^{63}Ni=6.5:1

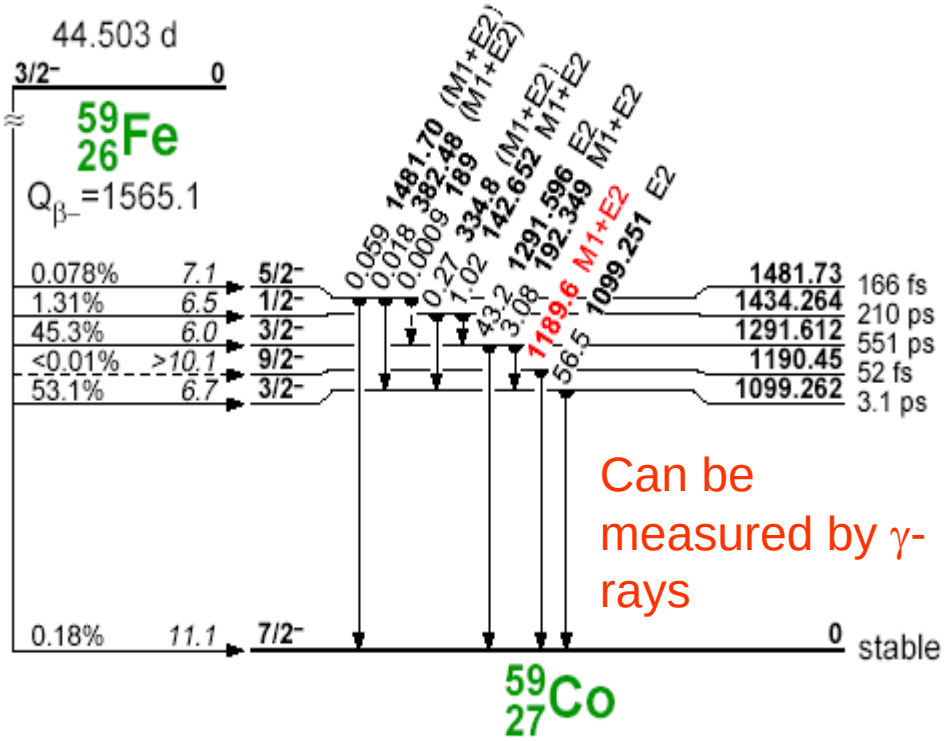
Activity ratio: ^{59}Ni/^{63}Ni=1:133

Other isotopes of Ni and Fe produced in Nuclear reactor

- Ni isotopes: ^{59}Ni,
  - ^{58}Ni(n, γ)^{59}Ni; ^{60}Ni(n,2n)^{59}Ni



- Fe isotopes: ^{59}Fe
  - ^{58}Fe(n, γ)^{59}Fe; ^{59}Co(n, p)^{59}Fe



Analytical method for ^{63}Ni and ^{55}Fe

- Due to their low energy of beta particle and measurable electrons, LSC is the most suitable method for their measurement.
- Due to their pure beta and EC decay, they have to be separated from matrix elements and all other radionuclides.

Mearement methods

^{55}Fe: X-ray spectrometry (<1%);

LSC (30-45%)

^{63}Ni: gas flow counting(anti-coincidence, <10-50%)

Ion implanted silicon detector (1-6%)

LSC (60-80%)

- Analytical procedure:
  - Decomposition of sample
  - Separation of Ni or Fe from matrix elements and all other radionuclides
  - Preparation of a suitable solution for LSC measurement.

Decomposition of samples

- Metals (steel, Ni-Cr-X alloy, Copper, Lead, Al alloy)
  - Acid degestion
- Concrete, soil, sediment
  - Alkali fusion followed by water leaching
  - Acid digestion
- Plants, organic materials, resin
  - Ashing followed by acid digestion
- Graphite
  - Ashing (800 ^{o}C) followed by acid leaching
  - Degestion with mixed acids (HNO_3+$HClO_4$+H_2SO_4) (it takes 3-4 hours)

Decomposition of graphite by ashing for determination of ^{63}Ni and ^{55}Fe

Temp °C	Ashing time	Carrier,mg		Degestion	Recovery, %	
		Fe	Ni		^{55}Fe	^{63}Ni
1100	3 min.	---	---	---	---	45%
800	2-3 h	…	…	HCl	96-98 %	97-99%
800	2-3 h	10	…	HCl	95-98%	90-95%
800	2-3 h	…	10	HCl	90-95%	95-98%
800	3 h	4	2	HCl	40-75%	30-65%
800	24 h	4	2	HCl+ $HClO_4$		30-45%
800	6 h	….	2	HCl+ $HClO_4$	80-85%	75-80%
800	3.5 h	4	2	HCl + $HClO_4$	92-95%	90-95%
800	3	10	5	HCl + $HClO_4$	91-95%	90-95%

- Ni and Fe is lost during ashing at:
  - Higher ashing temperature (>900 °C)
  - Longer ashing time
  - Add both Fe and Ni carrie and leaching just with HCl (this is due to a Fe-Ni compound formed which is difficult to be dissolved by HCl)
- Optimal ashing conditions:
  - 750-850 °C
  - Less than 3.5 hours
  - Leaching with HCl + $HClO_4$ or add Fe and Ni carrier individually or after ashing.

Interfering Radionuclides

Nuclide	Half-life	Decay	Nuclide	Half-life	Decay
^{60}Co	5.27 y	β^-,γ	^{3}H	12.33 y	β^-
^{58}Co	70.86 d	β^+, γ	^{14}C	5730 y	β^-
^{152}Eu	13.54 y	$\varepsilon, \beta^-,\gamma$	^{133}Ba	10.51 y	ε
^{154}Eu	8.59 y	β^-,γ	^{41}Ca	1.03E5 y	ε
^{51}Cr	27.7 d	ε,γ	^{36}Cl	3.01E5 y	β^-, ε
^{65}Zn	244.3 d	$\varepsilon, \beta^+, \gamma$	^{137}Cs	30.7 y	β^-
^{54}Mn	312.3 d	$\varepsilon, \beta^+, \gamma$	^{134}Cs	2.06 y	β^-,ε
^{151}Sm	90 y	β^-	^{90}Y	64 h	β^-
^{90}Sr	28.79 y	β^-			

Chemical Separation of Ni

1. From main matrix elements
2. From, Ba, Cl, Cs, Ca, Sr, etc.
3. From actinides
4. From Fe, Co, Cu, Mn, Zn etc.
5. From Cr, Eu, Cu, Co.

Chemical Separation of Fe

1. From main matrix elements
2. From, Ba, Cl, Cs, Ca, Sr, etc.
3. From actinides
4. from Ni, Co, Cu, Mn,Zn, Cr, Eu, etc.

Traditional methods for separation of Ni

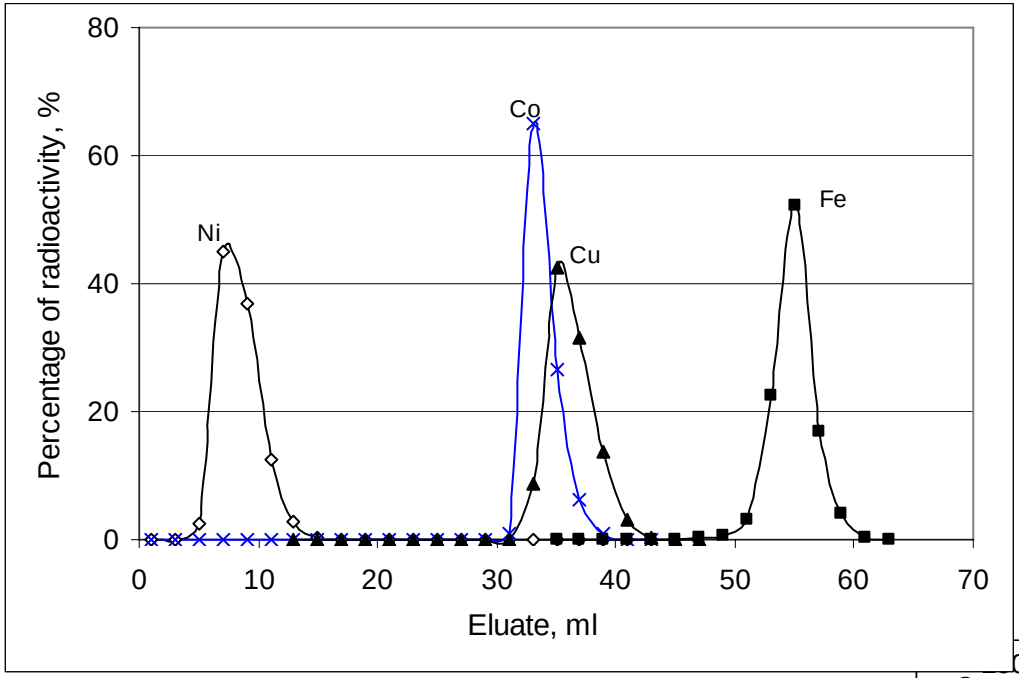
- Precipitation as $Ni(OH)_2$, separation from Sr, Cs, ^{3}H, ^{14}C, Ba, Ca, Cl.
- Precipition by ammonium, separate Ni from Fe, Mn, Eu, Pb, Al, Cr.
  - Low recovery of Ni in this method (Ni can be also partly precipitate in ammonium solution)
  - Cannot separate Cu, Co, etc.
- Ion exchange to separate Ni from Co, Cu, Zn, Fe, and transuranics.
- Precipitation or extraction of complex of Ni with dimethylglyoxime (DMG).
  - Co and Cu can also form a complex with DMG and extracted
- Evaporation of $Ni(CO)_6$

Separation of Fe and Ni by hydroxides precipitation

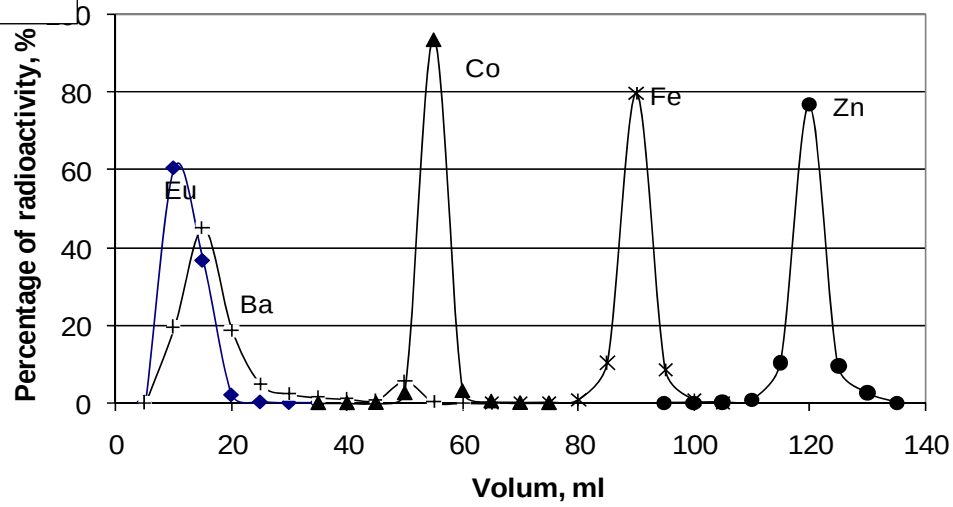
Element	Precipitation, %		Solution, %
	NaOH (pH9)	NH_4OH	NH_4OH
Fe^{3+}	>99.8	>99.8	<0.2
Ni^{2+}	>99.8	>20	< 80
Co^{2+}	>99.5	<20	< 80
Ba^{2+}	<30.5	<30.0	>70
Eu^{3+}	>99.8	>99.8	<0.2
Cs^{+}	<0.2	<0.2	>99.8
Sr^{2+}	<37.5	<35.0	>60

- Most of matrix in concrete and environmental samples, such as C, S, Ca, Si, Na will be separated.
- The recovery of Ni is not satisfied using ammonium to separate Ni from other matals by hydroxides precipitation
- Other metals such as Mn, Cr, V, Al, Pb, and transuranics will also be precipitated by NaOH, and cannot be separated from Ni and Fe.

Separation of Ni, Co, Eu, Ba by anion exchange chromatography



- **loading at 9 mol/l HCl, Ni is not absorbed on column, while others are absorbed.**
- **Removing Co, Cu by washing with 4 mol/l HCl**
- **Eluting Fe with 0.5 mol/l HCl**



Separation of Eu, Ba, Co by anion exchange chromatography, Bio-Rad AG1x4, 1x15 cm, 0-40ml:9M HCl, 40-70ml:4M HCl, 70-90ml, 0.05M HCl

Separation of Ni and Fe by anion exchange chromatography (conclusion)

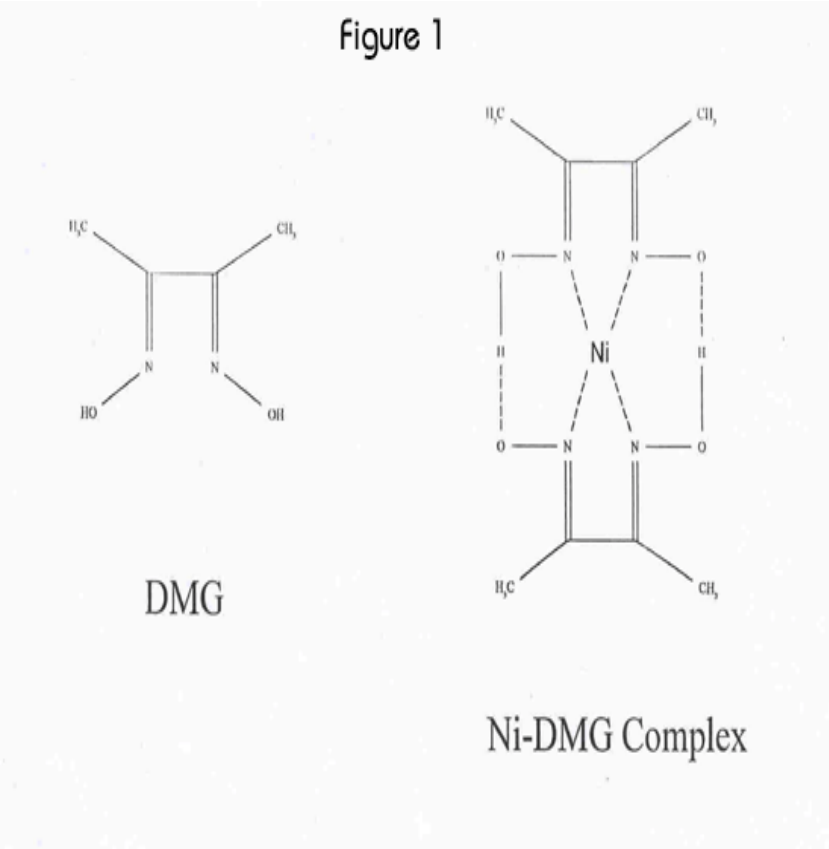
Element	Content, %	
	Ni fraction	Fe fraction
Fe^{3+}	<0.001	>98.5
Ni^{2+}	>99.5	<0.001
Co^{2+}	<0.01	<0.1
Ba^{2+}	<7.5	<0.001
Eu^{3+}	>99.8	<0.001
Cs^{+}	>99.5	<0.001
Sr^{2+}	>99.5	<0.001

- Ni can be completely separated from Fe, Co, Cu, Zn, U, Pu, etc.
- Fe can be separated from Ni, Cr, Mn, Th, etc.

- Ni cannot be efficiently separated from Cr, Eu, Sm, Mn, V, Sc, Ti, Zr, Ba, Th, Am. Of them, the radioisotopes of Eu, Sm, Ba, Zr, Mn, Cr and matrix elements of Cr, Mn V in metal and alloy seriously interfer the determination of Ni-63.
- Fe cannot be completely separated from Zn, Co, Cu, Pu, Np, especially when a large amount of Fe (>10 mg) is loaded on the column.

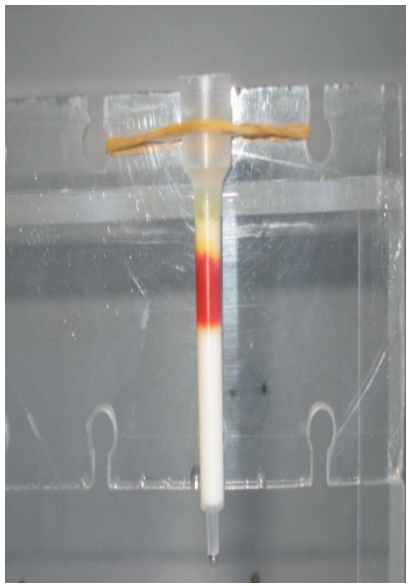
Thus: a further purification for both Ni and Fe is needed.

Separation of Ni using Ni-DMG complex



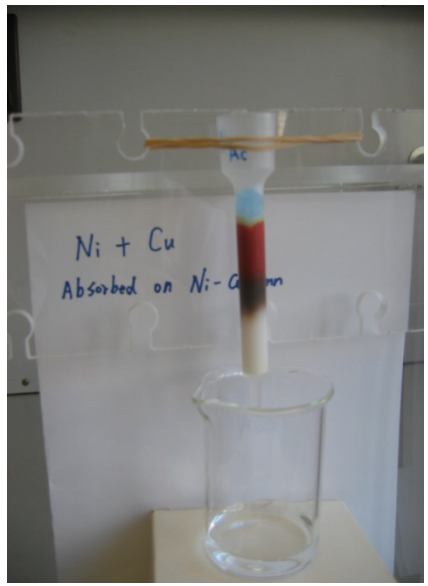
- Ni can form a stable specific complex with dimethylglyoxime. By Ni-DMG precipitation or organic solvent extraction of Ni-DMG complex at low concentration, Ni can be separated from many other elements.
- While, some other metals, such as Co, Cu can also form a complex with DMG and interferring the separation of Ni.

Formation of M-DMG complex



2mg Ni^{2+}

2mg Ni^{2+} +
2mg Co^{2+}

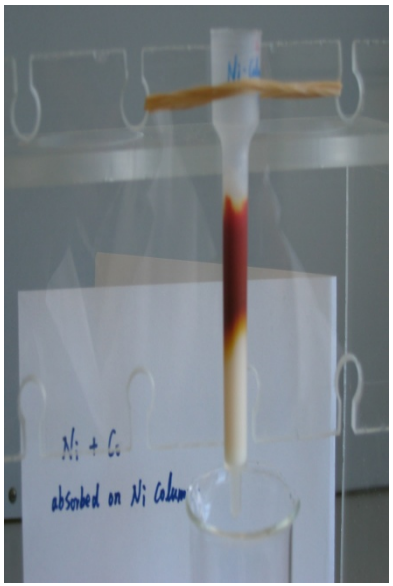


2mg Ni^{2+} +
2mg Cu^{2+}

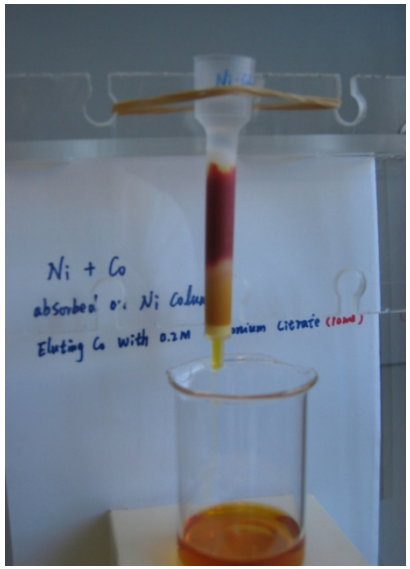
2mg Ni^{2+} +
8mg Fe^{3+}

Purification of Ni by specific Ni-extraction chromatography

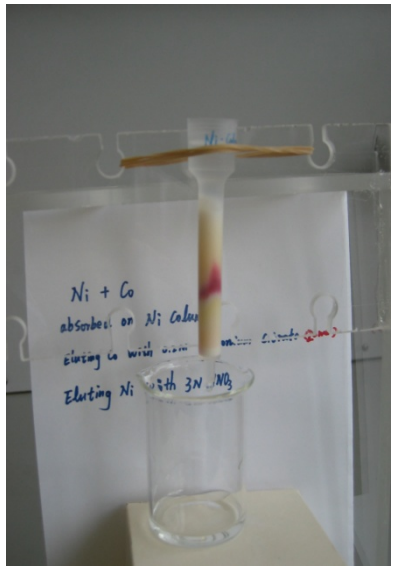
The Nickel Resin contains the DMG inside the pores of a polymethacrylate resin. The nickel-DMG precipitate occurs on the resin , where it is held and readily separated from other elements in the supernatant.



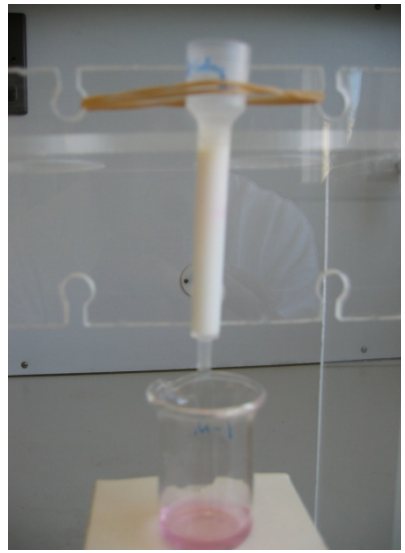
1. Loading of solution



2. Washing with 0.2 M ammonium citrate to remove other elements



3. Eluting Ni using HNO3



4. Evaporte eluted Ni-DMG solution to 0.1-0.2 ml for LSC

Purification of Ni by specific Ni-extraction chromatography (conclusion)

Element	Recovery or decontamination factor
Ni^{2+}	> 98.5%
Fe^{3+}	10^4
Co^{2+}	10^3
Ba^{2+}	10^4
Eu^{3+}	10^4
Cs^{+}	10^4
Sr^{2+}	10^4

Ni specific extraction chromatography has a higher decontamination to most of elements, such as Fe, Co, Cu, Cr. Mn, Ba, Eu, transuranics, etc.

•A higher recovery of Ni can be obtained in the procedure.

Separation of Fe by solvent extraction

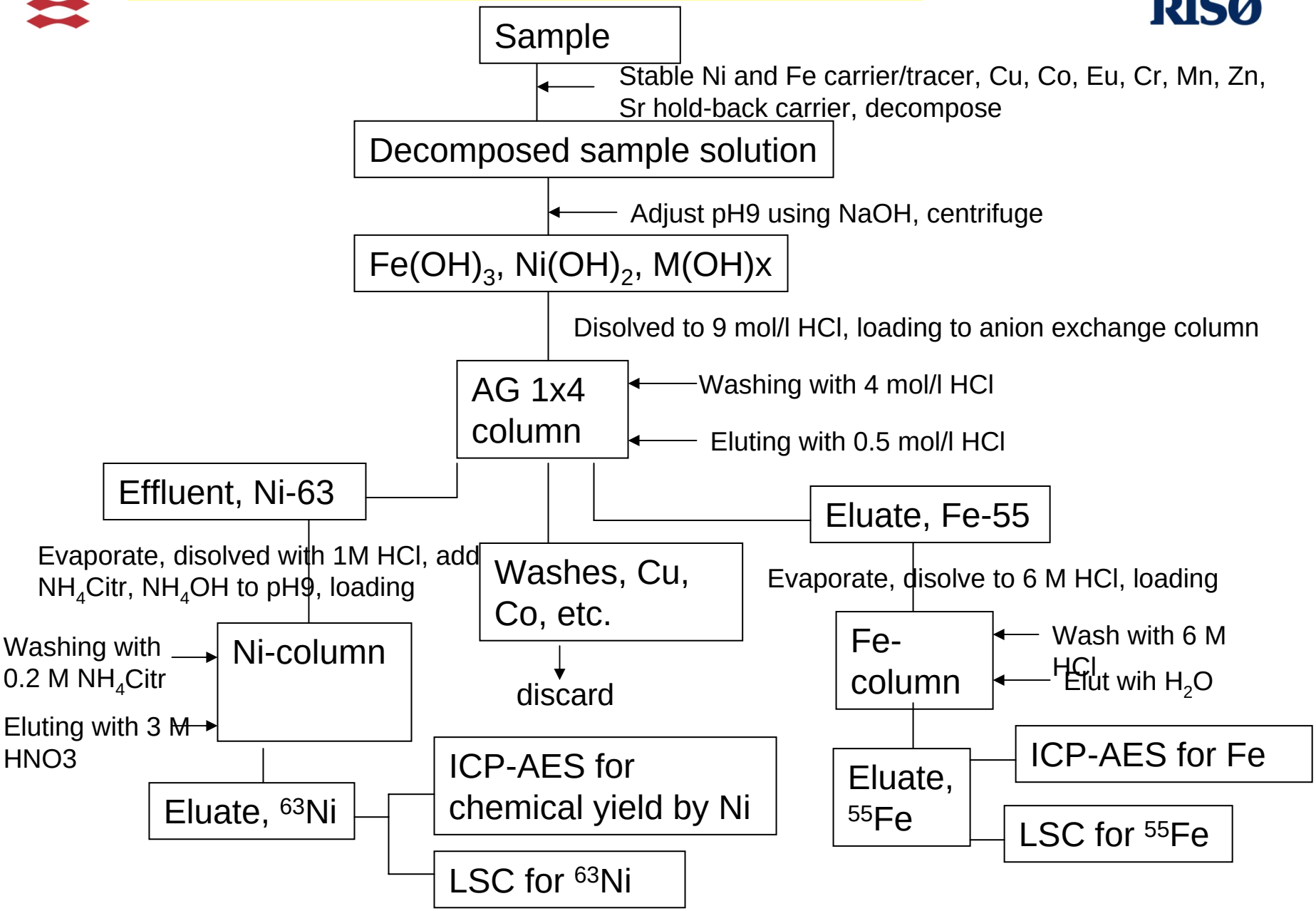
- Di-isopropyl ether (DIPE)
- Methyl-isobutyle (MIBK)
- Ethyl acetate
- Iso-pentanol
- 8-hydroxyquinoline
- Triisooctylamine(TIOA)
- …

Solvent	Medium	Distribution factor
Ethyl acetate	6 mol/l	65
DIBK	6 mol/l	38
DIPE	6 mol/l	4

Purification of Fe by extraction chromatography

Column	capacity	Fe-specific
TRU	3 mg	no
Silica-immobilised formylsalic acid	54 mg	no
XAD-7/DIBK	1700 mg	yes

Analytical procedure for ^{63}Ni and ^{55}Fe

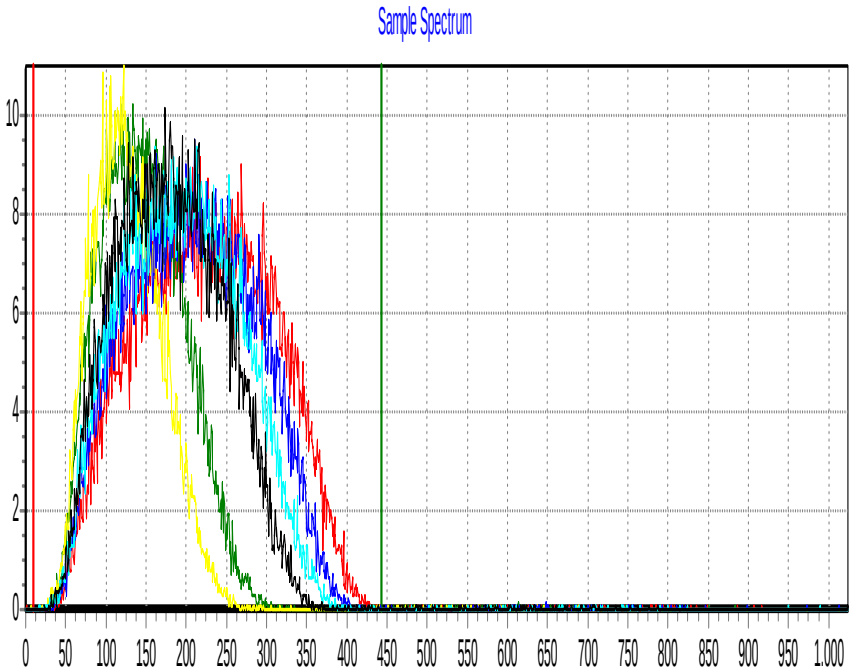


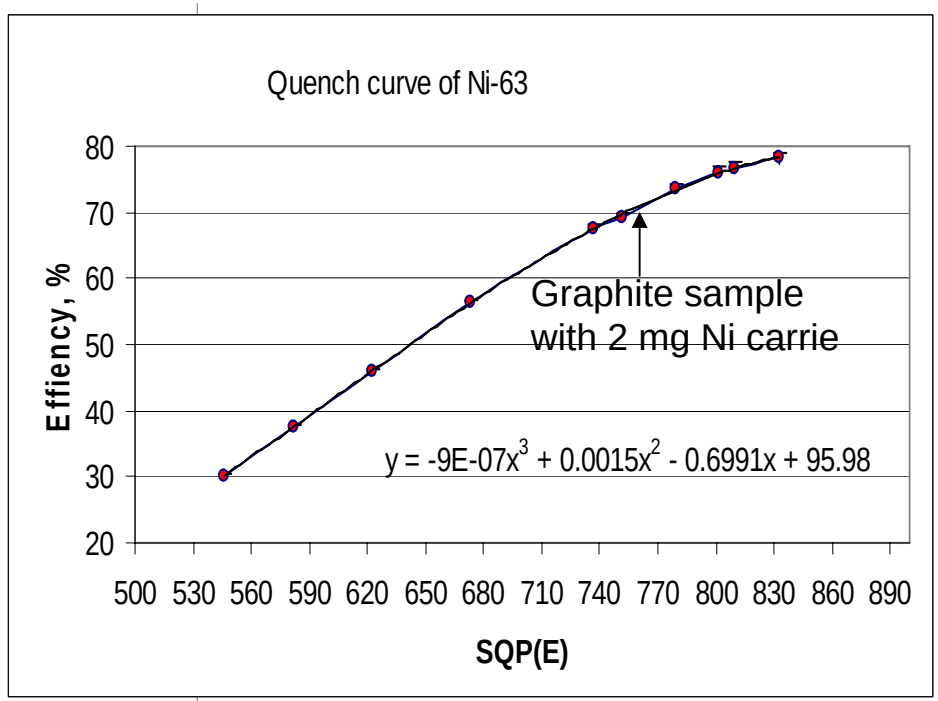
The recovery of Fe and Ni in the analytical procedure and decomtamination factors for main interferring radionuclides and elements

Interference	Recovery/decontamination factor		Interference	Recovery/decontamination factor	
	Fe fraction	Ni fraction		Fe fraction	Ni fraction
^{55}Fe	85-95%	$>10^5$	^{133}Ba	$>10^6$	$>10^5$
^{63}Ni	$>10^5$	80-95%	^{134,137}Cs	$>10^6$	$>10^6$
^{58,60}Co	$>10^5$	$>10^5$	^{89,90}Sr	$>10^6$	$>10^6$
^{152,154}Eu	$>10^6$	$>10^5$	^{41,45}Ca	$>10^6$	$>10^6$
^{151}Sm	$>10^6$	$>10^5$	^{36}Cl	$>10^6$	$>10^6$
^{54}Mn	$>10^5$	$>10^6$	^{3}H	$>10^6$	$>10^6$
^{51}Cr	$>10^6$	$>10^5$	^{14}C	$>10^6$	$>10^6$

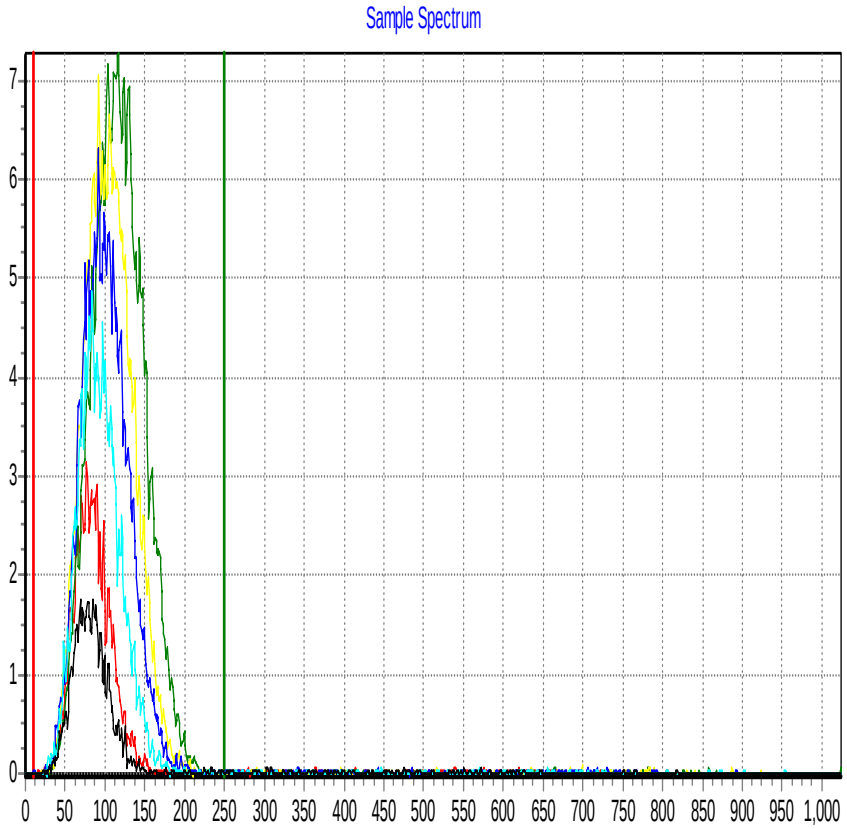
For all interferring radionuclides, the decontamination factors higher than 10^5.

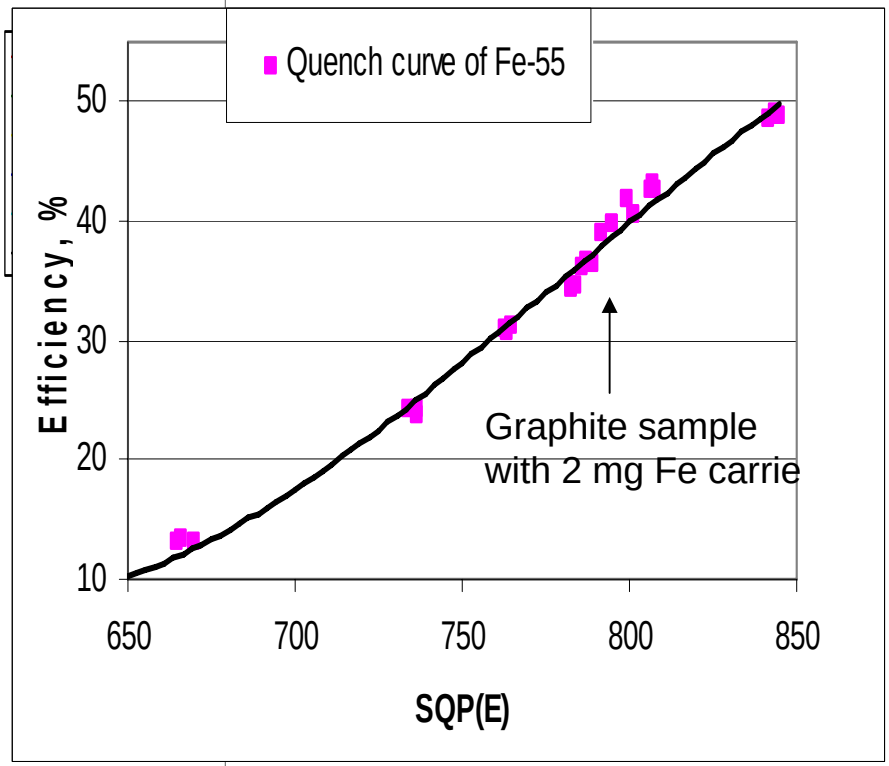
Quench correction for Ni-63



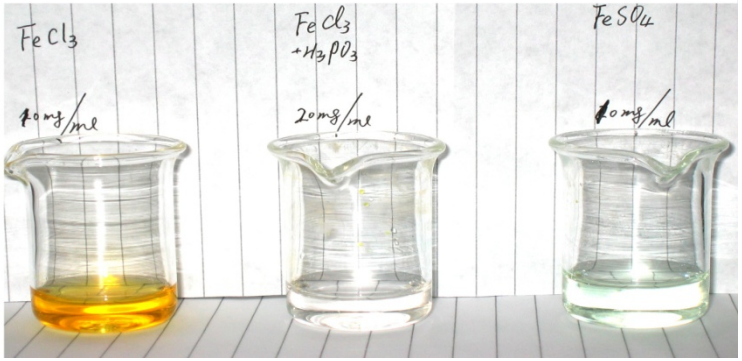


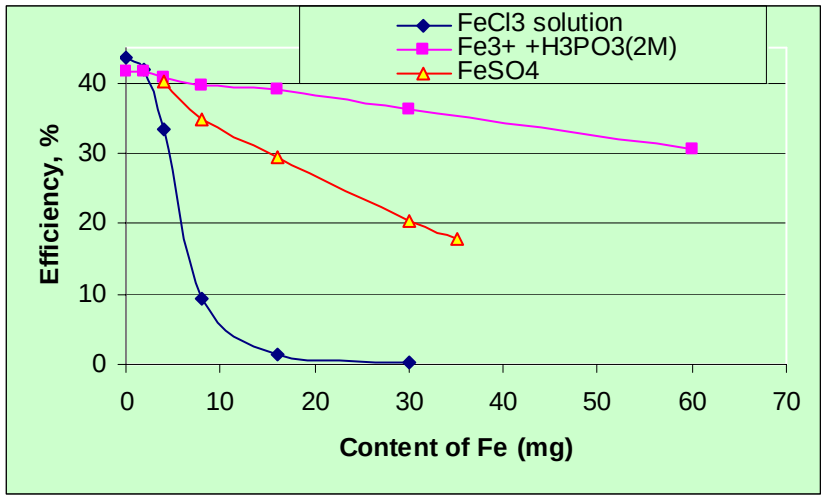
Quench correction for Fe-55





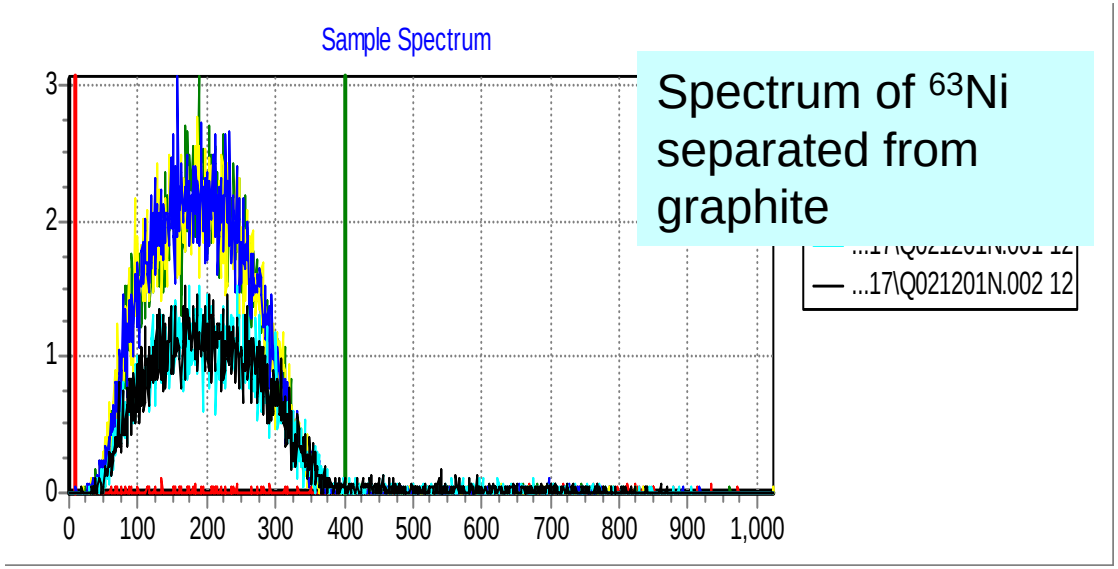
Preparation of separated ^{55}Fe for LSC



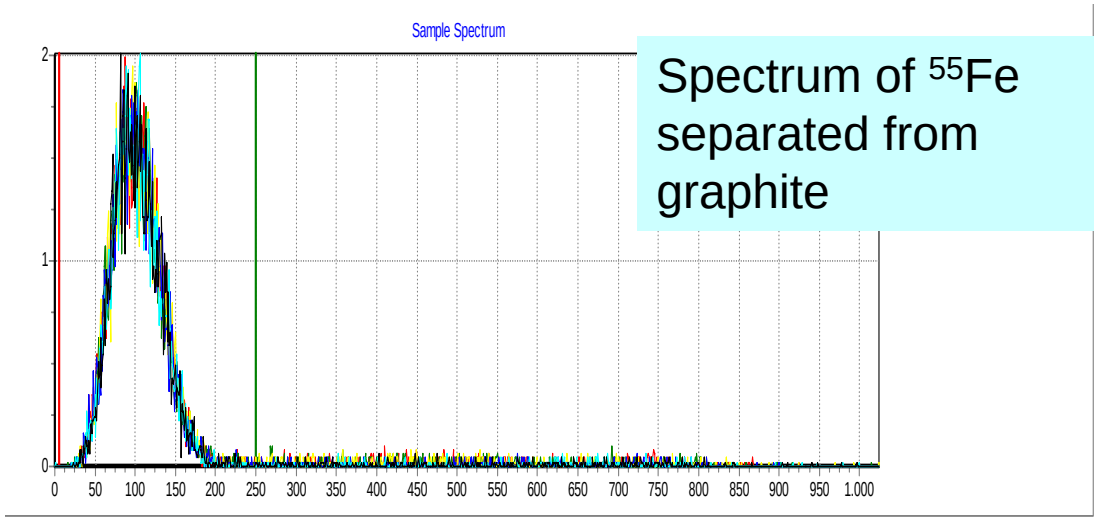


- Yellow colour Fe^{3+} is a very effective quenching agent
- Reduction of Fe^{3+} to Fe^{2+} using suitable reductant, such as ascorbic acid can reduce the quench, but Fe^{2+} is not stable and can be oxidize to Fe^{3+} again, and Fe^{2+} also has some colour quench.
- Solvent extraction of Fe^{3+} using some organic compounds such as di-2-ethylhexyl phosporic acid can reduce the Fe^{3+} colour quench, but not effective for large Fe content sample.
- In H_3PO_3 solution, a stable and colourless Fe-H_3PO_3 complex can be formed, therefore can significantly reduce the Fe^{3+} colour quench.
- H_3PO_3 as an acid has less quench and high solubility with scintillation cocktail, therefore can significantly improve the counting efficiency.
- As high as 40% counting efficiency of ^{63}Ni in 1.5 ml of 2 mol/l H_3PO_3 solution.
- The separated Fe was evaporated to dryness and then dissolved in 2 M H_3PO_3 solution in this work, for less than 10 mg Fe, 40% counting efficiency was obtained, and for 200 mg Fe, the efficiency is still as high as 13%.

Spectrum of ^{55}Fe and ^{63}Ni separated from samples



Spectrum of ^{63}Ni separated from graphite



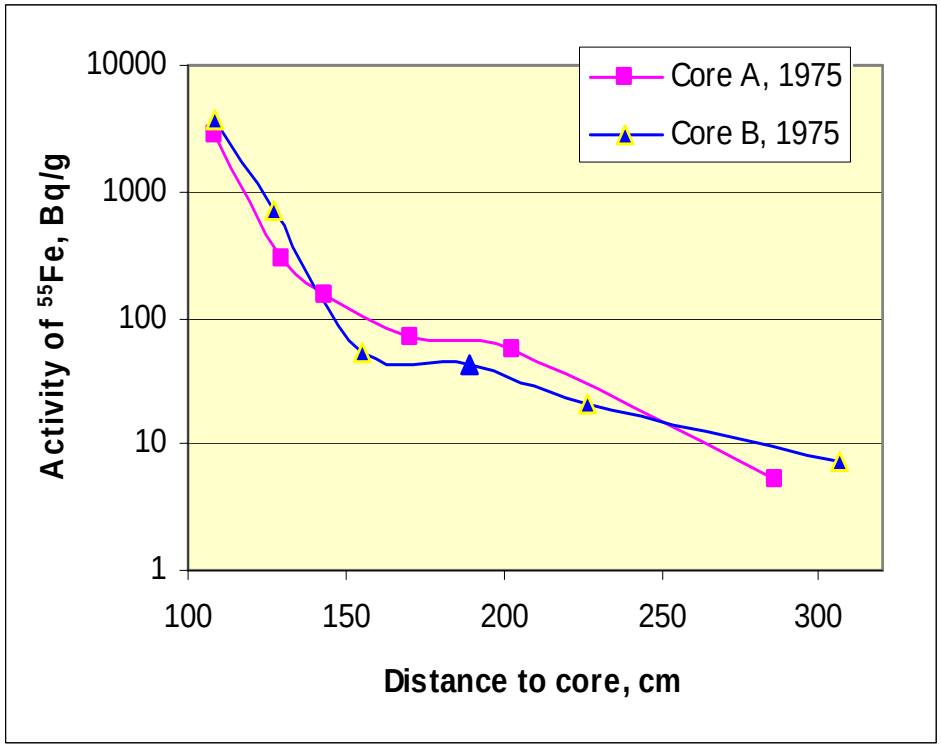
Spectrum of ^{55}Fe separated from graphite

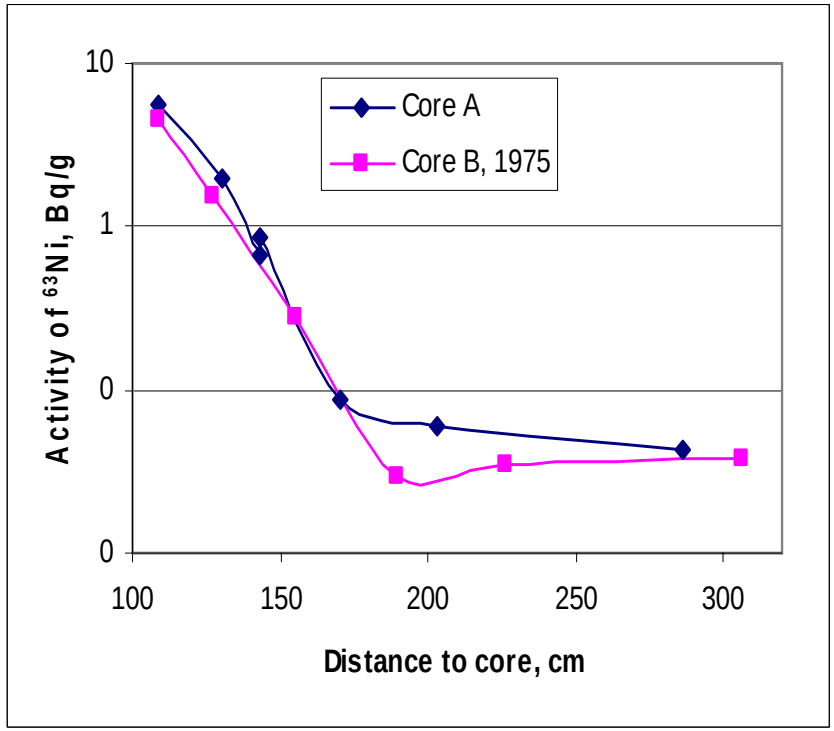
No interfence was found from other radionuclides in the ^{63}Ni and ^{55}Fe spectra, it indicates the decontamination from interference radionuclides is satisfied.

Determination of ^{63}Ni and ^{55}Fe in graphite samples

Sample No	Sample and Source	^{55}Fe		^{63}Ni	
		Recovery,%	Bq/g	Recovery,%	Bq/g
DR-3-T	Graphite from DR3	92.2	545000	94.63	5552
Ly7.5	Graphite from DR-2	90.4	0.53	93.89	92.5
Ly5.5	Graphite from DR-2	90.6	1.05	93.74	22.3
Yi7.5	Graphite from DR-2	92.5	1.92	93.35	7.71
Yi5.5	Graphite from DR-2	91.3	9.21	91.56	43.1
B-6	Heavy concrete from DR-2	92.3	0.015	90.34	0.022

^{63}Ni and ^{55}Fe in heavy concrete from DR-2





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Sumary

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- The oxidizer method is simple, rapid, accurate method for ^{3}H and ^{14}C in graphite, concrete samples. No significant cross contamination between ^{3}H and ^{14}C was observed.No significant interference from other radionuclides to the determination of ^{3}H and ^{14}C by this method
- A radiochemical separation procedure using hydroxides precipitation, anion exchange and extraction chromatography was developed for the determination of ^{63}Ni and ^{55}Fe in nuclear waste. The recoveries of Fe and Ni are 80-95%. The decontamination factors for most of interferring nuclides are higher than 10^{5} . The detection limit for ^{63}Ni and ^{55}Fe are 0.015 Bq and 0.035 Bq respectively.
- The method has been sucessfully used for the analysis of graphite and concrete from Danish reactors.